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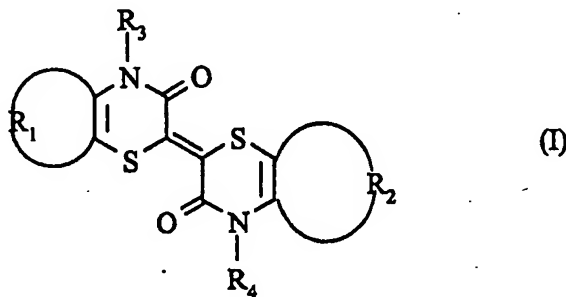
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09B 7/00, 67/22, C08K 5/46, C09D 11/00		A1	(11) International Publication Number: WO 98/32800
			(43) International Publication Date: 30 July 1998 (30.07.98)
(21) International Application Number: PCT/IB98/00109		(81) Designated States: AU, BG, BR, CA, CN, CZ, HU, IL, JP, KR, LT, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 28 January 1998 (28.01.98)			
(30) Priority Data:		Published With international search report.	
9701784.2	29 January 1997 (29.01.97)	GB	
9709193.8	7 May 1997 (07.05.97)	GB	
9716159.0	1 August 1997 (01.08.97)	GB	
2869/97	12 December 1997 (12.12.97)	CH	
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(54) Title: THIAZINE INDIGO PIGMENTS, SOLID SOLUTIONS THEREOF AND THEIR PREPARATION

(57) Abstract

New compounds according to the formula (I), wherein R₁ and R₂ are independently the atoms necessary to complete the formation of a substituted or unsubstituted aromatic or aliphatic carbocyclic or heterocyclic ring system and R₃ and R₄ have the meaning indicated in claim 1, a new process for the preparation of such a compound, solid solutions and mixtures comprising such a compound and the use of a compound of formula (I) as a pigment.



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THIAZINE INDIGO PIGMENTS, SOLID SOLUTIONS THEREOF AND THEIR PREPARATION

This invention relates to thiazine indigo pigments, solid solutions thereof and to a process of forming such pigments and solid solutions.

Thiazine indigo compounds are an important series of pigments. Prior art processes for forming these pigments involve the reaction of certain o-aminomercapto- carbocycles or heterocycles with maleic acid or a derivative thereof in the presence of a solvent. The solvents useful for this purpose were recognized to be either a carboxylic acid (which also acted to catalyze the reaction) or an inert polar aprotic solvent.

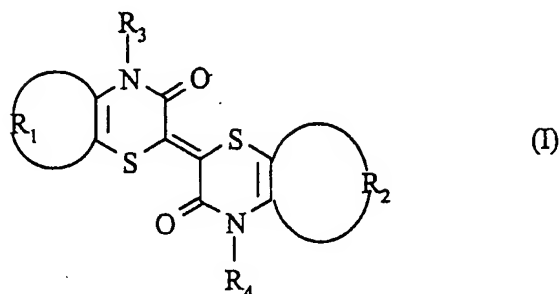
Thus in DE 2 151 723 a process is described for making certain symmetrically substituted benzothiazine indigo compounds wherein certain substituted ortho-aminomercapto- carbocycles or heterocycles are reacted with a maleic acid derivative in a carboxylic acid, e.g. acetic acid. The pigments formed in this way are produced in good yield but they exhibit dull shades. By symmetrically substituted is meant that there is identical substitution on each of the thiazine rings.

In DE OS 25 36 120 a process is described for making certain other symmetrically substituted benzothiazine indigo compounds wherein certain substituted ortho-aminothiophenols are reacted with a maleic acid derivative in an inert polar aprotic solvent. The benzothiazine indigo compounds formed, allegedly display improved pigmentary properties, e.g. brighter and cleaner shade over the compounds made in a carboxylic acid solution, however, they can only be produced in poor yield.

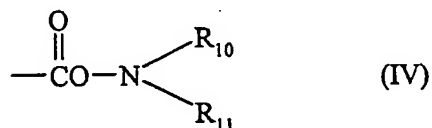
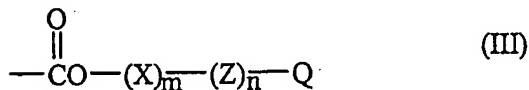
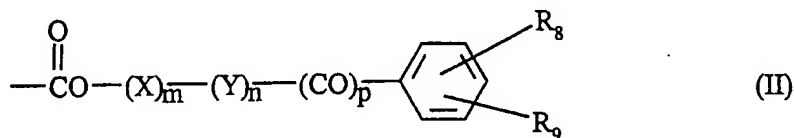
There remains a need to provide further thiazine indigo pigments and an improved process of forming thiazine indigo pigments.

It has now been found that new thiazine indigo pigments can be formed in high yield and which exhibit pigmentary properties which are better than heretofore achieved.

The invention provides in one of its aspects a pigment which is a compound according to the formula (I)



wherein R_1 and R_2 are independently the atoms necessary to complete the formation of a substituted or unsubstituted aromatic or aliphatic carbocyclic or heterocyclic ring system, the radicals R_3 and R_4 , independently of each other, are hydrogen or a group of the formulae (II), (III) or (IV)

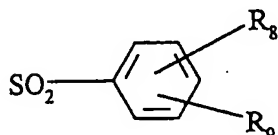


whereby in the formulae (II), (III) and (IV)

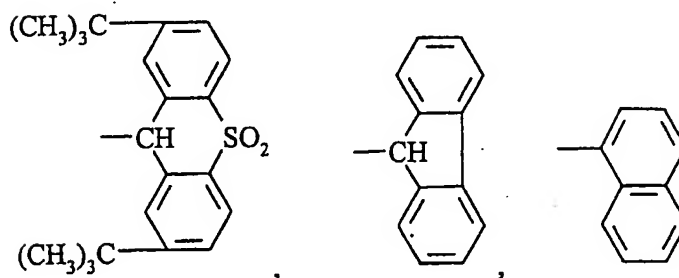
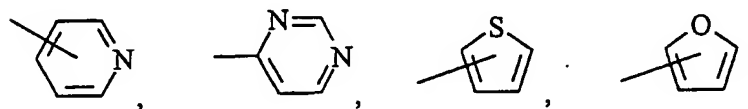
- | | |
|---------------------|--|
| m , n und p , | independently of each other, are zero or 1; |
| X | C_{1-14} -alkylen or C_{2-8} -alkenylen; |
| Y | a group $-V-(CH_2)_q-$; |
| Z | a group $-V-(CH_2)_r-$; |
| V | C_{3-6} -cycloalkylen; |
| q | a number of 1 to 6; and |
| r | a number of zero to 6, |

R_8 and R_9 independently of each other, signify hydrogen, C_{1-6} -alkyl, C_{1-4} -alkoxy, halogen, CN, NO_2 , unsubstituted phenyl or phenoxy, phenyl or phenoxy substituted by C_{1-4} -alkyl, C_{1-4} -alkoxy or halogen;

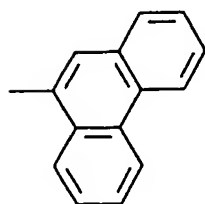
Q hydrogen, CN, $Si(R_8)_3$, a group $C(R_{12})(R_{13})(R_{14})$, in which R_{12} , R_{13} and R_{14} are halogen; a group



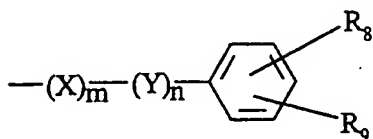
in which R_8 and R_9 have the above meaning; a group SO_2-R_{15} or SR_{15} , in which R_{15} is C_{1-4} -alkyl; a group $CH(R_{16})_2$, in which R_{16} is unsubstituted phenyl or phenyl substituted by C_{1-4} -alkyl, C_{1-4} -alkoxy or halogen; or a group of the formula



or



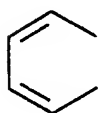
R_{10} and R_{11} independently of each other, signify hydrogen, C_{1-18} -alkyl, a group



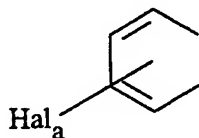
in which X, Y, R_8 , R_9 , m and n have the above meaning, or
 R_{10} and R_{11} , together with the nitrogen atom to which they are bound, build a pyrrolidinyl-, piperidinyl- or morpholinylrest,

provided that, if R_3 and/or R_4 are a group of the formula (III), Q is hydrogen and n is zero, m must be 1 and X a C_{2-14} -alkylen- or C_{2-8} -alkenylengroup which is branched at the carbon atom bound to oxygen, and if both R_3 and R_4 are hydrogen, R_1 and R_2 cannot be identical.

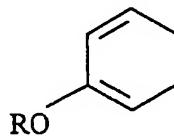
Preferably R_1 and R_2 are independently selected from the residues consisting of



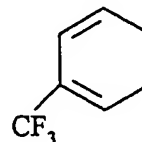
(a)



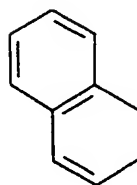
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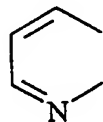
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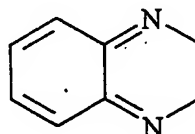
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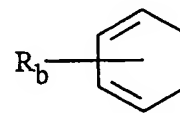
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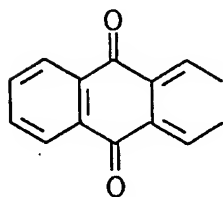
(f)



(g)



(h)



(i)

wherein Hal is halogen which includes F, Cl and Br, especially Cl

R is C₁₋₄ alkyl especially methyl or ethyl

a is 1, 2, 3 or 4

b is 1, 2, 3 or 4

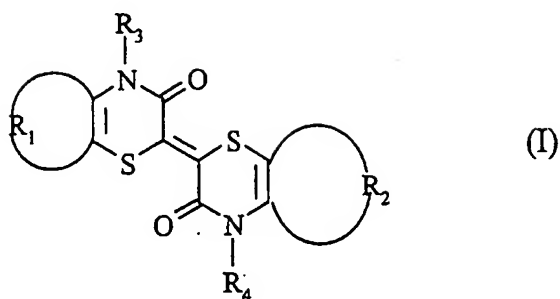
In a preferred pigment according to the invention R₁ is a residue which consists of the atoms necessary to complete a benzene ring which is optionally substituted with, for example halogen or alkyl and R₂ consists of the atoms necessary to complete a ring system which is a differently substituted benzene ring or a different substituted or unsubstituted aromatic or aliphatic carbocyclic or heterocyclic ring system, e.g. naphthalene, pyridine or 1,4-benzodiazine.

The pigments may be substituted on the ring systems with one or more of any of the non-water-solubilising substituents common in the art of pigments. Preferably the ring system substituents are selected from the group consisting of halogen, trifluoromethyl, nitro, cyano, alkyl, alkoxy, amino, alkylamino, thioalkyl, phenoxy, phenylamino, phenylthio, acyl, acyloxy or acylamino.

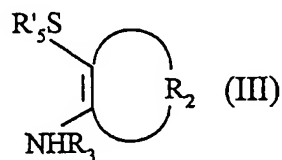
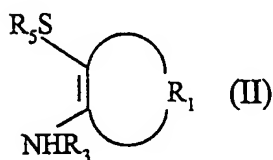
The term "halogen" includes fluorine and especially chlorine and bromine. The term "alkyl" or "alkoxy" includes said functionality having from 1 to 4 carbon atoms. The terms "alkylamino" and "phenylamino" include N,N-dialkylamino and N,N-diphenylamino as well as N-monoalkylamino and N-monophenylamino.

The aforementioned alkyl, alkoxy, phenyl and phenoxy substituents may themselves contain one or more substituents selected from the substituents hereinabove described.

The invention provides in one of its further aspects a process of forming thiazine indigo pigments according to the formula (I)

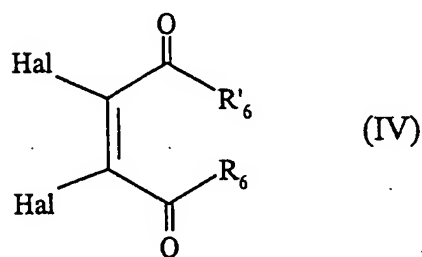


wherein R_1 and R_2 are independently the atoms necessary to complete the formation of a substituted or unsubstituted aromatic or aliphatic carbocyclic or heterocyclic ring system, R_3 and R_4 are hydrogen, comprising the step of reacting in the presence of a solvent system comprising a carboxylic acid and an inert polar aprotic solvent, a compound of formula (II) and a compound of formula (III)



wherein R_5 and R'_5 independently are H or a metallic ion selected from Na^+ , K^+ or Zn^{2+}

with a compound of formula (IV)



wherein Hal is Cl or Br, R_6 and R'_6 independently of the other is a leaving group commonly used in substitution reactions at carbonyl carbon atoms, e.g. Cl or alkoxy or together X and X' represent an oxygen atom. A compound of formula (IV) shown in its cis-form above may also be used in its trans-form.

Preferably the molar ratio of the reactants is 1:1:1.

The process is carried out in the presence of a carboxylic acid, e.g. acetic acid, which also acts as a catalyst, and an inert polar aprotic solvent, e.g. xylene or a xylene mixture, nitrobenzene, chlorobenzene, dimethylformamide, or dimethylacetamide, in particular dimethylformamide, dimethyl acetamide or N-methylpyrrolidone. The reaction is preferably carried out in solvent system which consists of 5 to 95% by weight of carboxylic acid, e.g. acetic acid, more preferably 10% by weight and 95 to 5% by weight of polar aprotic solvent, more preferably 90% by weight.

The reaction temperature is preferably of the order of 60 to 200°C

The thiazine indigo pigments produced by the above process may be symmetrically substituted, that is R_1 and R_2 as well as R_3 and R_4 are identical. Alternatively, they may be asymmetrically substituted, that is, R_1 and R_2 or R_3 and R_4 are not identical. Non-identity refers to either the ring systems R_1 and R_2 being different or, in the event that the ring systems are identical, the substituents attached to the respective ring systems are different. The asymmetrical compounds are novel compounds.

Thiazine indigo pigments according to formula (I) in which at least one of the substituents R_3 and R_4 is not hydrogen, are produced by reacting the pigments of formula (I) in which both R_3 and R_4 are hydrogen, with a dicarbonate of formula (V)



or with a trihaloacetic acid ester of the formula (VI)



or with a mixture of dicarbonate of the formula (V) and a dicarbonate of the formula (VII)



or with a mixture of trihaloacetic acid ester of the formula (VI) and a trihaloacetic acid ester of the formula (VIII)



or with an azide of the formula (IX)



which can also be used as a mixture 1:1 with an azide of the formula (X)



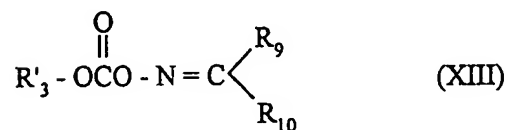
or with a carbonate of the formula (XI)



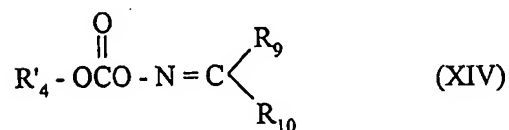
which can also be used as a mixture 1:1 with a carbonate of the formula (XII)



or with an alkylideneiminooxyformic acid ester of the formula (XIII)



which can also be used as a mixture 1:1 of the formula (XIV)



whereby in the formulae (V), (VI), (VII), (VIII), (IX), (X), (XI), (XII), (XIII) and (XIV)

R'_3 and R'_4 have the meanings of R_3 and R_4 except hydrogen,

R_7 means chlorine, fluorine or bromine,

R_8 is C_{1-4} alkyl, unsubstituted phenyl or phenyl substituted by halogen, C_{1-4} alkyl, C_{1-4} alkoxy or -CN,

R_9 is -CN or -COOR₈, and

R_{10} is unsubstituted phenyl or phenyl substituted by halogen, C_{1-4} alkyl, C_{1-4} alkoxy or -CN

in an aprotic organic solvent in the presence of a base as a catalyst. Preferably such reaction is performed at temperatures from zero to 200°C, more preferably from 10 to 100°C, and lasts from 2 to 48 hours.

The invention also provides a solid solution or a mixture of a thiazine indigo pigment according to formula (I) and another pigment of the class comprising diketopyrrolo-pyrrole, quinacridone, anthraquinone, benzimidazole, naphthole AS, azo condensation, isoindolinone, isoindoline, perylene, dioxazine, indigo, thioindigo, metal complex, perinone, quinophthalone and phthalocyanine pigments.

The portion of the thiazine indigo pigment in said solid solutions or mixtures can vary between 20 and 80 % by weight, in particular between 30 and 70 % by weight, especially between 40 and 60 % by weight. The preferred pigments according to formula (I) are those indicated above and most preferred pigments are those according to formula (I) in which R_1 and R_2 are the residues consisting of the atoms necessary to complete a benzene ring which is optionally substituted with, for example halogen or alkyl.

Another aspect of the present invention is a method for preparing said solid solutions or mixtures by synthesizing and/or finishing one of said pigments in the presence of the other. So it is possible to synthesize a pigment of formula (I) in the presence of the other pigment, or the other pigment is synthesized in the presence of a thiazine indigo pigment of formula (I). The conditions of synthesizing the pigments of formula (I) are described above. Especially, the reactants and the other pigments are employed in such portions as to yield a solid solution or mixture as described above.

Alternatively, the solid solutions and/or the mixtures of a thiazine-indigo pigment and another pigment can be prepared by dissolving the pigments in an appropriate solvent like dimethylsulfoxide or an alcohol, in the presence of sodium hydroxide or potassium hydroxide or sodium alcoholate or potassium alcoholate, and precipitating the pigment in water or a mixture of water and an alcohol, or adding water or a mixture of water and an alcohol into the alkaline solution of pigments. One can also use organic or inorganic acids in the precipitation step.

Another way to prepare solid solutions and/or the mixtures of a thiazine-indigo pigment and another pigment, is to dissolve partially or completely a thiazine-indigo pigment and another pigment in sulfuric acid or concentrated sulfuric acid, or polyphosphoric acid, at temperatures from 0°C to 200°C, and to precipitate the pigment particles by adding water or a mixture of water and an alcohol, or by pouring the acidic medium in ice or water or a mixture of water and an alcohol. One can also use additives known in the state-of-the-art to control the particle size of the pigment.

The thiazine indigo pigments formed by a process according to the invention are suitable for the mass pigmentation of suitable substrates including synthetic polymers, synthetic resins and regenerated fibers optionally in the presence of solvents. These substrates more particularly include oil, water and solvent based surface coatings, polyester spinning melts, polyethylene, polystyrene and polyvinyl chloride molding materials, rubber and synthetic leather. Furthermore, the pigments can be used in the manufacture of printing inks, for the mass coloration of paper and for coating and printing textiles.

When applied to the afore-mentioned substrates the thiazine indigo pigments are found to be resistant to migration and fast to light, and show fastness to washing, chlorite, hypochlorite and peroxide bleaching, rubbing, overspraying and solvents. Notably, the pigments display high tinctorial power, good opacity and good heat stability.

Based on the polymeric material to be mass dyed the thiazine indigo pigments according to the invention are used in amounts of 0.01 to 30% by weight, preferably of 0.1 to 10% by weight.

Of particular interest is the capability of compounds according to formula (I) in which R_3 and/or R_4 are different from hydrogen, to be transformed into compounds according to formula (I) in which R_3 and R_4 both are hydrogen. This can be achieved by thermal treatment (heating at temperature from 50 to 400°C, preferably from 100 to 200°C, or irradiation with laser beam), by photolytic treatment (irradiation with light of wave length under 375 nm) or chemical treatment with organic or inorganic acids or bases, whereby the solids, solutions or dispersions containing such pigments in organic or aqueous carriers, polymeric solutions or melts are treated and the various treatments can be combined. This means that lacquers, printing inks (especially for ink jet) and plastics, e.g. in fiber form can be mass dyed with compounds in masked form which are then transformed into the pigments in free form. Such application allows to obtain such mass dyed substrates with superior qualities regarding purity, dyeing strength, brilliance and transparency.

It is also possible to prepare a solid solution or a mixture of thiazine-indigo pigments according to formula (I) and another pigment of the class previously listed, especially of the class of diketopyrrolopyrrole, quinacridone or thiazine-indigo, by decomposing the carbamate of a thiazine-indigo pigment in the presence of the carbamate of another pigment. Alternatively, the carbamate of the thiazine-indigo pigment is added and decomposes in the preparation of the other pigment. One can also prepare a solution of carbamates in an organic solvent and initiate the decomposition by adding an acid catalyst or a basic catalyst or by heating.

The transformations can be carried out in an inert solvent such as xylene or a xylene mixture, nitrobenzene, chlorobenzene, dimethylformamide, dimethylacetamide or N-methylpyrrolidone.

There now follows a series of examples which serve to illustrate the invention.

EXAMPLE 1

To a solution of 25g (0.15 mol) of dichloromaleic anhydride in 250 ml of dimethylformamide and 20 ml of acetic, kept below 25°C by an external water bath, are added in portions 47g (0.15 mol) of o-aminothiophenol zinc salt, over two hours. The yellow suspension so formed

is gradually heated up to 130°C, over 24 hours. The red-orange suspension is filtered hot, washed with dimethylformamide and ethanol. The orange solid is dried at 80°C under vacuum. 37.4g (76.5%) of an orange pigment are isolated.

COMPARATIVE EXAMPLE X

(Reaction carried out in acetic acid solution according to a prior art process)

Following the procedure described in DE 2 151 723 or in Helvetica Chimica Acta 57 (8), 2264-78 (1974), a mixture of 73g (0.23 mol) of 2-aminothiophenol zinc salt and 35.4g (0.21 mol) of dichloromaleic anhydride in 850 ml of acetic acid, is heated at reflux for 24 hours. The red suspension is filtered hot, washed with hot acetic acid, ethanol and water. The orange solid is dried at 80°C under vacuum. 54.1g of an orange solid are isolated. This crude pigment is heated in 300 ml of dimethylformamide at 100°C for 2 hours and filtered hot, washed with dimethylformamide and ethanol. 49.6g (72.1%) of orange pigment are isolated, after drying at 80°C under vacuum.

COMPARATIVE EXAMPLE Y

(reaction carried out in a polar aprotic solvent according to a prior art process)

Following the procedure described in DE 2 536 120, a mixture of 29.6g (0.095 mol) of 2-aminothiophenol zinc salt and 17.4g (0.1 mol) of dichloromaleic anhydride in 150 ml of dimethylformamide, is heated up to 130°C. The mixture is stirred overnight at 130°C. The red suspension is filtered hot, washed with hot dimethylformamide, ethanol and water. The orange solid is dried at 80°C under vacuum. 16.1g (54.8%) of an orange pigment are isolated.

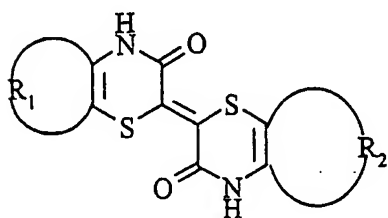
EXAMPLE 2

Preparation of asymmetric benzothiazine indigo compound


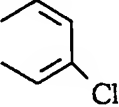

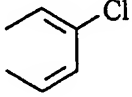
To a solution of 25g (0.15 moles) of dichloromaleic anhydride in 250ml of dimethylformamide and 20ml of acetic acid are added, in portions over 1 hour, 23.53g (0.075 moles) of o-aminothiophenol zinc salt. During the addition, the temperature of the reaction mixture is maintained below 25°C by means of a water bath. Thereafter, 25.6g (0.075 moles) of 2-amino-5-methylthiophenol zinc salt are added in portions over a 1 hour period. The resultant yellow suspension is gradually heated to 130°C and maintained at this temperature


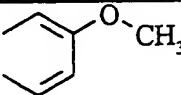

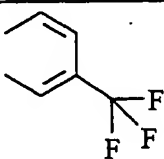

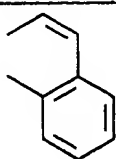



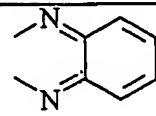
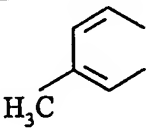
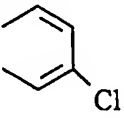
for 24 hours. The resultant red-orange suspension is filtered hot, and washed with dimethylformamide and ethanol. The remaining red-orange solid is dried at 80°C under vacuum. 40.3g (79%) of a brilliant orange pigment are isolated.

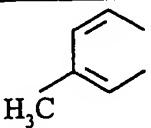
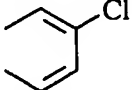
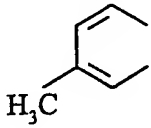
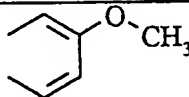
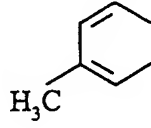
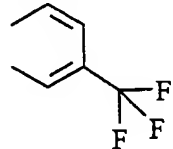
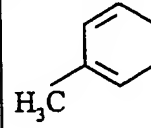
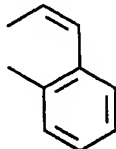
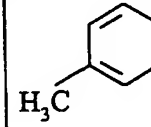
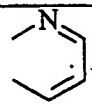
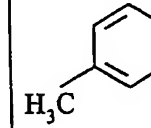
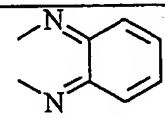
EXAMPLES 3 - 26

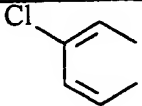
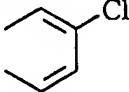
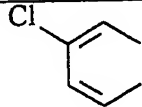
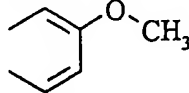
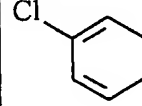
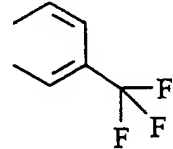
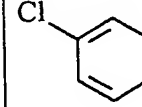
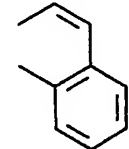
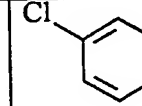

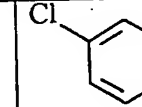
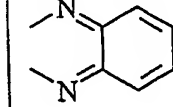


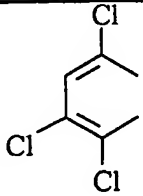
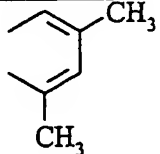
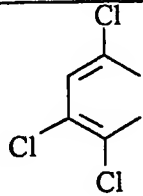
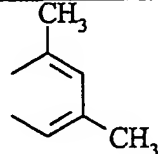
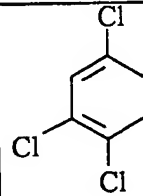
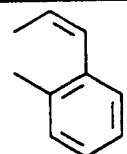
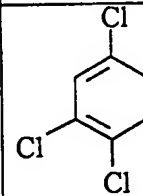
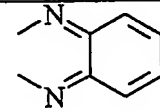
The compounds of Examples 3 to 26 are synthesised according to a process described in Example 2 using the appropriate starting materials.

Example	R ₁	R ₂	Hue in PVC
3			Orange
4			Orange

5			Orange
6			Yellow
7			Orange
8			Orange
9			Orange
10			Orange

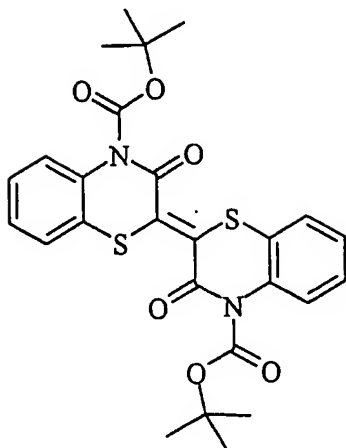
11			Orange
12			Orange
13			Yellow
14			Red
15			Orange
16			Orange

17			Red
18			Orange
19			Yellow
20			Red
21			Orange
22			Red

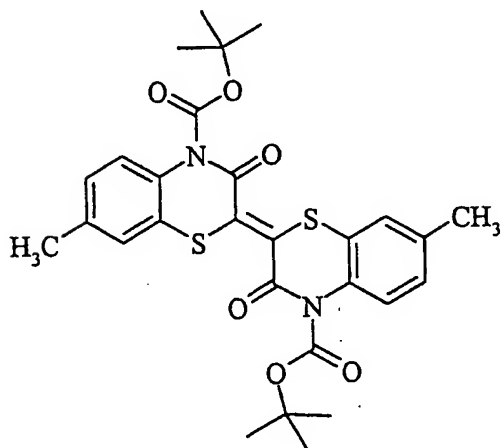
23			Red
24			Orange
25			Red
26			Red

EXAMPLE 27

A suspension of 30g trans-2,2'-bis(4H-1,4-benzothiazine)-indigo in 350ml N,N-dimethylformamide is mixed with 2,8g 4-dimethylaminopyridine and then 42,2g di-tert-butyl-dicarbonate is added. The mixture is stirred at ambient temperature under exclusion of atmospheric humidity. After 6 hours again 31g di-tert-butyl-dicarbonate are added and during 16 hours the stirring continued. The precipitated yellow product is filtrated, washed with 40ml N,N-dimethylformamide and 300ml methanol and dried in vacuum at ambient temperature. One obtains 43,5g of the product with the formula

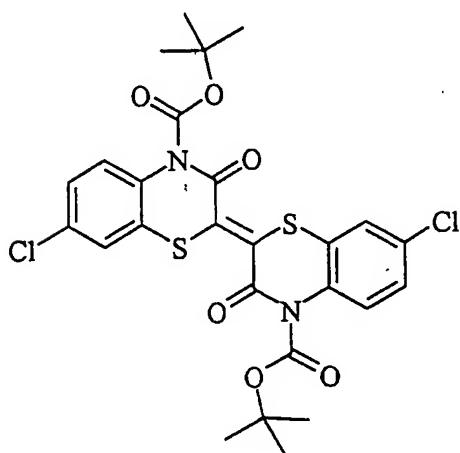
**EXAMPLE 28**

A suspension of 35,4g 7,7'-dimethyl-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo in 250ml N,N-dimethylformamide are mixed with 3,3g 4-dimethylaminopyridine and then 45,8g di-tert-butyl-dicarbonate are added. The mixture is stirred at ambient temperature under exclusion of atmospheric humidity. After 6 hours again 45,8g di-tert-butyl-dicarbonate are added and during 16 hours the stirring continued. The precipitated yellow product is filtrated, washed with 50ml N,N-dimethylformamide and 400ml methanol and dried in vacuum at ambient temperature. One obtains 53,5g of the product with the formula

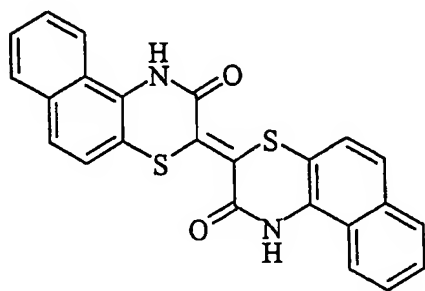


EXAMPLE 29

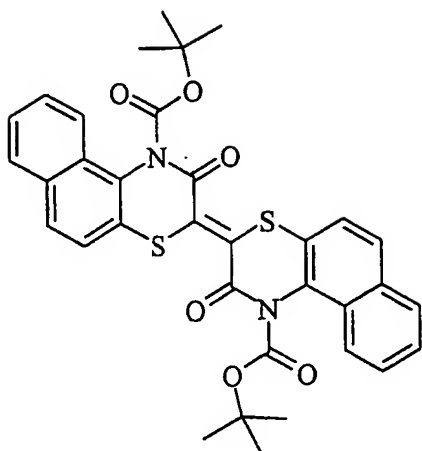
A suspension of 22,12g 7,7'-dichloro-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo in 300ml N,N-dimethylformamide are mixed with 1,78g 4-dimethylaminopyridine and then 26,8g di-tert-butyl-dicarbonate are added. The mixture is stirred at ambient temperature under exclusion of atmospheric humidity. After 6 hours again 26,8g di-tert-butyl-dicarbonate are added and during 16 hours the stirring continued. The precipitated yellow product is filtrated, washed with 50ml N,N-dimethylformamide and 130ml methanol and dried in vacuum at ambient temperature. One obtains 30g of the product with the formula

**EXAMPLE 30**

In an analogous manner, when using trans-2,2'-bis(4H-1,4-naphthothiazine)-indigo of the formula



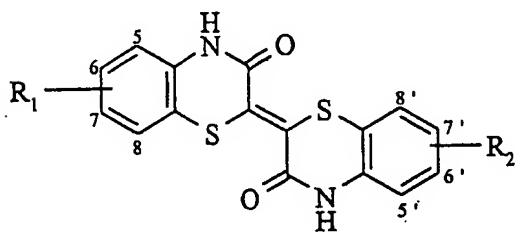
the corresponding trans-2,2'-bis(4H-1,4-naphthothiazine)-indigo of the formula



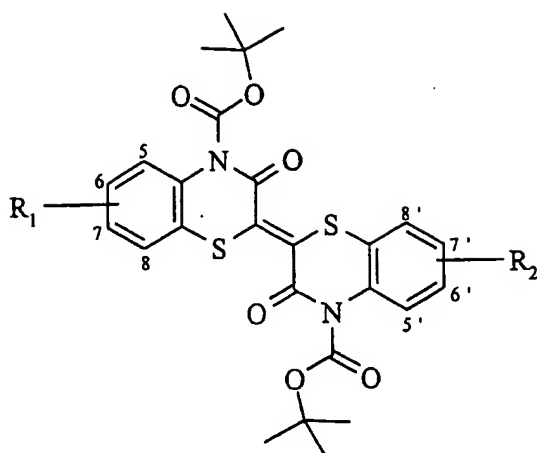
can be produced. 4,7g of the product are obtained.

EXAMPLES 31-33

In an analogous manner, when using trans-2,2'-bis(4H-1,4-benzothiazine)-indigo compounds of the formula



in which R_1 and R_2 have the meaning indicated in columns 2 and 3 of the following table, corresponding trans-2,2'-bis(4H-1,4-benzothiazine)-indigo compounds of the formula



are produced.

TABLE

Example	R ₁	R ₂	Results
31	6-Cl	6'-Cl	92,1%
32	7-CH ₃	7'-Cl	86%
33	6-Cl	7'-CH ₃	95,6%

EXAMPLE 34

0,520g N,N'-bis(tert.-butoxycarbonyl)-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from Example 27 are heated during 40 minutes at 200°C in a reaction vessel. One obtains 0,318g of an orange powder. The analytical data of the powder correspond to those of pure trans-2,2'-bis(4H-1,4-benzothiazine)-indigo.

EXAMPLE 35

A mixture of 3,16g N,N'-bis(tert.-butoxycarbonyl)-trans-2,2'-bis(4H-1,4-benzo-thiazine)-indigo from Example 27 and 11,4g toluene-4-sulfonic acid-monohydrate in 75ml N,N-dimethylformamide is heated to 100°C under stirring, stirring is continued at this temperature for 4 hours and then the mixture is allowed to cool down to room temperature. The precipitated pigment is filtrated, washed first with 25ml N,N-dimethylformamide then with

75ml methanol and dried in vacuum at 90°C. One obtains 1,8g of a red-orange powder. The analytical data of the powder correspond to those of pure trans-2,2'-bis(4H-1,4-benzothiazine)-indigo. The yield of the transformation amounts to 92%.

EXAMPLE 36

A mixture of 3,32g N,N'-bis(tert.-butoxycarbonyl)-7,7'-dimethyl-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from Example 28 and 11,4g toluene-4-sulfonic acid-monohydrate in 75ml N,N-di-methylformamide is heated to 100°C under stirring, stirring is continued at this temperature for 4 hours and then the mixture is allowed to cool down to room temperature. The precipitated pigment is filtrated, washed first with 35ml N,N-dimethylformamide then with 75ml methanol and dried in vacuum at 90°C. One obtains 2,0g of an orange powder. The analytical data of the powder correspond to those of pure 7,7'-dimethyl-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo. The yield of the transformation amounts to 97%.

EXAMPLE 37

A mixture of 5g N,N'-bis(tert.-butoxycarbonyl)-7,7'-dichloro-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from Example 29 and 4g toluene-4-sulfonic acid-monohydrate in 150ml N,N-dimethylacetamide is heated to 100°C under stirring, stirring is continued at this temperature for 4 hours and then the mixture is allowed to cool down to room temperature. The precipitated pigment is filtrated, washed first with 35ml N,N-dimethylacetamide then with 100ml methanol and dried in vacuum at 90°C. One obtains 3,0g of a red powder. The analytical data of the powder correspond to those of pure 7,7'-dichloro-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo. The yield of the transformation amounts to 90%.

EXAMPLE 38

1,05g N,N'-bis(tert.-butoxycarbonyl)-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from Example 27 are stirred in 20ml acetone. Then 2ml HCl 30% are added at once. The mixture is stirred during 7 hours under reflux and then cooled to 30°C. The precipitated pigment is filtrated, washed first with 50ml acetone, then with 20ml methanol and dried in vacuum at 90°C. One obtains 0,466g of an orange powder. The analytical data of the powder correspond to those of pure trans-2,2'-bis(4H-1,4-benzothiazine)-indigo.

EXAMPLE 39

1,11g N,N'-bis(tert.-butoxycarbonyl)-7,7'-dimethyl-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from Example 28 are stirred in 20ml acetone. Then 2ml HCl 30% are added at once. The mixture is stirred during 23 hours under reflux and then cooled to 30°C. The precipitated pigment is filtrated, washed first with 50ml acetone, then with 50ml methanol and dried in vacuum at 90°C. One obtains 0,625g of an orange powder. The analytical data of the powder correspond to those of pure 7,7'-dimethyl-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo.

Each of the pigments (obtained according to Examples 1 to 39) are milled following a known procedure. A 500 ml glass flask is filled with 10g of pigment, 30g of NaCl, 150 ml of acetone and 500g of glass beads having a diameter of 0.6 to 0.9 mm. The flask is closed and rotated on a roller mill for 72 hours. The glass beads are separated, the pigment suspension is filtered and washed with 2 liters of water. The pigment is dried at 80°C under vacuum before testing.

EXAMPLE 40

Co-synthesis of benzothiazine-indigo with 3,6-di(4-chlorophenyl)-1,4-diketopyrrolo-[3,4,c]-pyrrole: 80 / 20

A reactor of 500 ml is charged with 150 ml of dimethylformamide and 15 ml of acetic acid, then 16.7 g (0.1 mol) of dichloromaleic anhydride, and 6.1 g of 3,6-di(4-chlorophenyl)-1,4-diketopyrrolo-[3,4,c]-pyrrole. 15.65 g (0.05 mol) of o-aminothiophenol zinc salt is added over 45 min, keeping the temperature below 20°C. A further 15.65 g (0.05 mol) of zinc salt is added over 30 min. The resultant red suspension is gradually heated to 135°C and the temperature maintained for 12 hours. The red suspension is filtered hot, and washed with dimethylformamide and ethanol. The red solid is dried at 80°C under vacuum. 29.12 g of a red pigment is isolated. A 500 ml glass flask is filled with 10 g of the crude pigment, 30 g of NaCl, 150 ml of acetone and 500 g of glass beads having a diameter of 0.6 to 0.9 mm. The flask is closed and rotated on a roller mill for 16 hours. The glass beads are separated, the pigment suspension is diluted with water, filtered and washed with 2 liters of water. The pigment is dried at 80°C under vacuum, and ground before testing.

EXAMPLE 41

Co-synthesis of benzothiazine-indigo with 3,6-di(4-chlorophenyl)-1,4-diketopyrrolo-[3,4,c]-pyrrole: 50 / 50

A reactor of 500 ml is charged with 150 ml of dimethylformamide and 15 ml of acetic acid, then 11.7 g (0.07 mol) of dichloromaleic anhydride, and 17.11 g of 3,6-di(4-chlorophenyl)-1,4-diketopyrrolo-[3,4,c]-pyrrole. 10.96 g (0.035 mol) of o-aminothiophenol zinc salt is added over 45 min, keeping the temperature below 20°C. A further 10.96 g (0.035 mol) of zinc salt is added over 30 min. The resultant red suspension is gradually heated to 135°C and the temperature maintained for 12 hours. The red suspension is filtered hot, and washed with dimethylformamide and ethanol. The red solid is dried at 80°C under vacuum. 27.4 g of a red pigment is isolated. A 500 ml glass flask is filled with 10 g of the crude pigment, 30 g of NaCl, 150 ml of acetone and 500 g of glass beads having a diameter of 0.6 to 0.9 mm. The flask is closed and rotated on a roller mill for 16 hours. The glass beads are separated, the pigment suspension is diluted with water, filtered and washed with 2 liters of water. The pigment is dried at 80°C under vacuum, and ground before testing.

EXAMPLE 42

Co-synthesis of benzothiazine-indigo with 2,9-dimethylquinacridone: 80 / 20

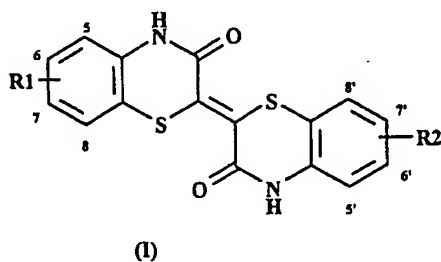
A reactor of 500 ml is charged with 150 ml of dimethylformamide and 15 ml of acetic acid, then 16.7 g (0.1 mol) of dichloromaleic anhydride, and 6.1 g of 2,9-dimethylquinacridone. 15.65 g (0.05 mol) of o-aminothiophenol zinc salt is added over 45 min, keeping the temperature below 20°C. A further 15.65 g (0.05 mol) of zinc salt is added over 30 min. The resultant red suspension is gradually heated to 135°C and the temperature maintained for 12 hours. The red suspension is filtered hot, and washed with dimethylformamide and ethanol. The red solid is dried at 80°C under vacuum. 25 g of a red pigment is isolated. A 500 ml glass flask is filled with 10 g of the crude pigment, 30 g of NaCl, 150 ml of acetone and 500 g of glass beads having a diameter of 0.6 to 0.9 mm. The flask is closed and rotated on a roller mill for 16 hours. The glass beads are separated, the pigment suspension is diluted with water, filtered and washed with 2 liters of water. The pigment is dried at 80°C under vacuum, and ground before testing.

EXAMPLE 43**Co-synthesis of benzothiazine-indigo with β -quinacridone: 80 / 20**

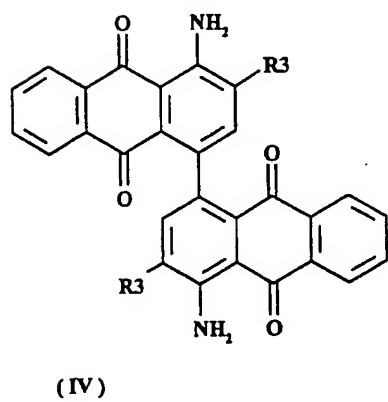
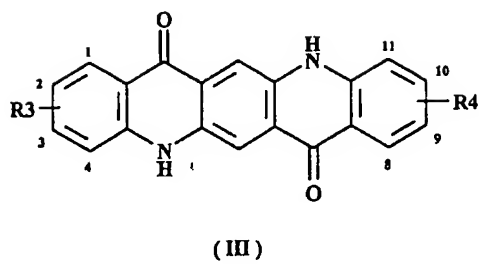
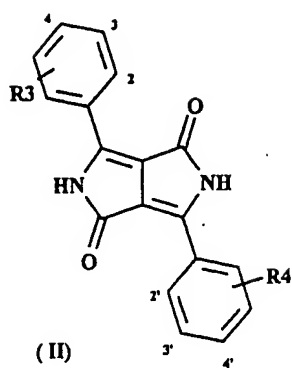
A reactor of 500 ml is charged with 150 ml of dimethylformamide and 15 ml of acetic acid, then 16.7 g (0.1 mol) of dichloromaleic anhydride, and 6.1 g of β -quinacridone. 15.65 g (0.05 mol) of o-aminothiophenol zinc salt is added over 45 min, keeping the temperature below 20°C. A further 15.65 g (0.05 mol) of zinc salt is added over 30 min. The resultant red suspension is gradually heated to 135°C and the temperature maintained for 12 hours. The red suspension is filtered hot, and washed with dimethylformamide and ethanol. The red solid is dried at 80°C under vacuum. 26 g of a red pigment is isolated. A 500 ml glass flask is filled with 10 g of the crude pigment, 30 g of NaCl, 150 ml of acetone and 500 g of glass beads having a diameter of 0.6 to 0.9 mm. The flask is closed and rotated on a roller mill for 16 hours. The glass beads are separated, the pigment suspension is diluted with water, filtered and washed with 2 liters of water. The pigment is dried at 80°C under vacuum, and ground before testing.

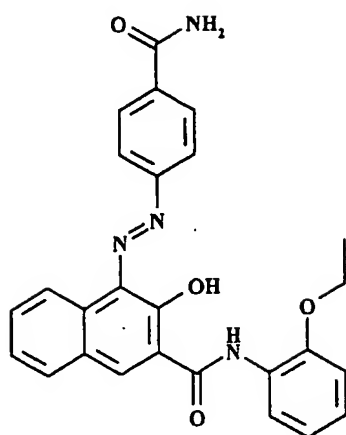
EXAMPLES 44-100

Co-synthesis and/or Solid solutions of thiazine-indigos (I),

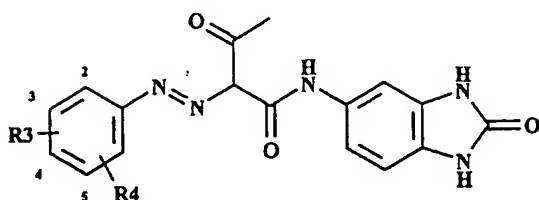


with pigments of following structures (II), (III), (IV), (V), (VI), (VII), (VIII) or (IX):

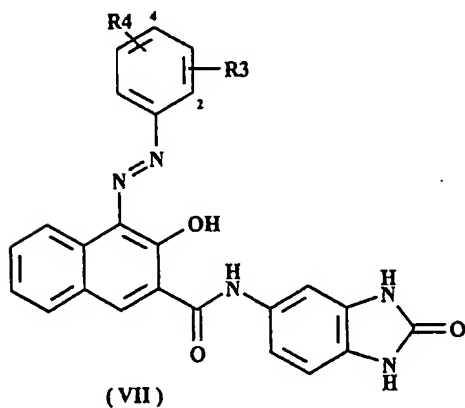




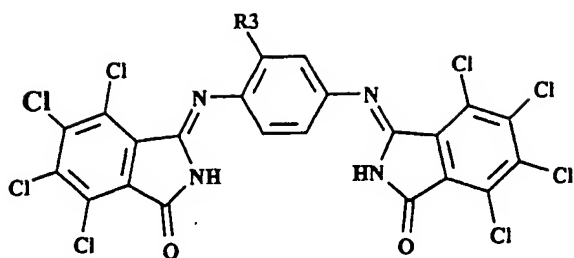
(V)



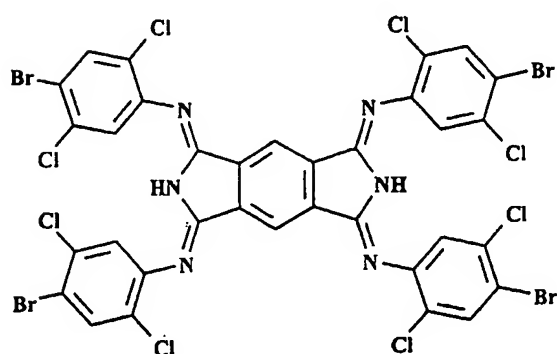
(VI)



(VII)



(VIII)



(IX)

are prepared according to the process described in the previous examples 40-43, adjusting the amount of pigment introduced in the beginning to reach the expected ratio between thiazine-indigo and the other pigment. They are listed in the following table.

Ex.	Thiazine-indigo	Other	pigment	Ratio	Hue in lacquers	
		structure	(II)			
	R ₁	R ₂	R ₃	R ₄		
44	H	H	4-Cl	4'-Cl	80/20	red scarlet
45	"	"	4-Cl	4'-Cl	50/50	red
46	"	"	3-CN	3'-CN	80/20	orange
47	"	"	3-CN	3'-CN	50/50	red
48	7-CH ₃	7'-CH ₃	4-Cl	4'-Cl	80/20	red
49	"	"	4-CL	4'-Cl	50/50	red
50	"	"	3-CN	3'-CN	80/20	orange
51	"	"	4-terButyl	4'-terButyl	50/50	orange

52	7-Cl	7'-Cl	4-Cl	4'-Cl	80/20	red
53	"	"	4-Cl	4'-Cl	50/50	red
54	"	"	3-CN	3'-CN	80/20	red
55	"	"	3-CN	3'-CN	50/50	red
			structure	(III)		
	R₁	R₂	R₃	R₄		
56	H	H	H	H	80/20	red
57	"	"	H	H	50/50	red
58	"	"	2-CH ₃	9-CH ₃	50/50	red
59	"	"	2-Cl	9-Cl	80/20	red
60	7-CH ₃	7'-CH ₃	H	H	50/50	red
61	"	"	2-CH ₃	9-CH ₃	50/50	red
62	"	"	2-Cl	9-Cl	80/20	red
63	7-Cl	7'-Cl	H	H	50/50	red
64	"	"	2-CH ₃	9-CH ₃	80/20	red
65	"	"	2-Cl	9-Cl	80/20	red
			structure	(IV)		
	R₁	R₂	R₃	R₄		
66	H	H	H	H	50/20	reddish orange
67	"	"	Br	Br	80/20	red
68	"	"	Br	Br	50/50	red
69	7-CH ₃	7'-CH ₃	H	H	50/50	red
70	"	"	Br	Br	50/50	red
71	7-Cl	7'-Cl	H	H	80/20	red
72	"	"	Br	Br	80/20	red
73	"	"	Br	Br	50/50	red
	R₁	R₂	structure	(V)		
74	H	H	"	"	80/20	red
75	"	"	"	"	50/50	red scarlet
76	7-CH ₃	7'-CH ₃	"	"	50/50	reddish orange
77	"	"	"	"	20/80	red

78	7-Cl	7'-Cl	"	"	80/20	red
79	"	"	"	"	50/50	red
			structure	(VI)		
	R₁	R₂	R₃	R₄		
80	H	H	3-COOCH ₃	5-COOCH ₃	80/20	orange
81	"	"	2-COOCH ₃	5-COOCH ₃	80/20	orange
82			2-NO ₂	4-Cl	50/50	orange
83	7-CH ₃	7'-CH ₃	3-COOCH ₃	5-COOCH ₃	80/20	yellow
84	"	"	2-COOCH ₃	5-COOCH ₃	80/20	yellow
85	"	"	2-NO ₂	4-Cl	50/50	orange
86	7-Cl	7'-Cl	3-COOCH ₃	5-COOCH ₃	80/20	orange
87	"	"	2-COOCH ₃	5-COOCH ₃	80/20	orange
88	"	"	2-NO ₂	4-Cl	50/50	reddish orange
			structure	(VII)		
	R₁	R₂	R₃	R₄		
89	H	H	2-COOCH ₃	H	50/50	red
90	"	"	2-OCH ₃	4-CONHC ₆ H ₅	80/20	red
91	7-CH ₃	7'-CH ₃	2-COOCH ₃	H	50/50	red
92	"	"	2-OCH ₃	4-CONHC ₆ H ₅	80/20	red
93	7-Cl	7'-Cl	2-COOCH ₃	H	50/50	red
94	"	"	2-OCH ₃	4-CONHC ₆ H ₅	80/20	red
			structure	(VIII)		
	R₁	R₂	R₃	R₄		
95	H	H	H		80/20	yellow
96	7-CH ₃	7'-CH ₃	H		50/50	yellow
97	7-Cl	7'-Cl	Cl		30/70	yellow
	R₁	R₂	structure	(IX)		
98	H	H	"	"	80/20	yellow
99	7-CH ₃	7'-CH ₃	"	"	50/50	yellow
100	7-Cl	7'-Cl	"	"	30/70	yellow

EXAMPLE 101

A mixture of 8,93 g of N,N'-bis(tert-butoxycarbonyl)-7,7'-dichloro-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from example 29 and 7,89 g of N,N'-bis(tert-butoxycarbonyl)-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from example 27 in 160 ml of N,N'-dimethylacetamide, is heated up to 110°C and stirred at this temperature for 2 hours. The solid is filtered at 60°C, washed with 100 ml of dimethylacetamide and 100 ml of methanol, then dried at 90°C under vacuum. 10 g of a red powder are obtained.

EXAMPLE 102

A mixture of 7,32 g of N,N'-bis(tert-butoxycarbonyl)-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from example 27 and 7,89 g of N,N'-bis(tert-butoxycarbonyl)-1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (prepared according to EP 0648770) in 150 ml of N-methylpyrrolidone is heated to 80°C. The solution of the carbamates is then heated to 135°C and stirred at this temperature for 2 hours. The solid is filtered at 60°C, washed with 125 ml of dimethylformamide and 100 ml of methanol, then dried at 90°C under vacuum. 7,2 g of a dark red powder are obtained.

EXAMPLE 103

A mixture of 6,25 g of N,N'-bis(tert-butoxycarbonyl)-7,7'-dichloro-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from example 29 and 6,03 g of N,N'-bis(tert-butoxycarbonyl)-1,4-diketo-3,6-di(4-chlorophenyl)-pyrrolo[3,4-c]pyrrole (prepared according to EP 0648770) in 150 ml of dimethylacetamide is heated to 60°C. 8 g of para-toluenesulfonic acid monohydrate are added and the mixture is heated to 110°C and stirred at this temperature for 4 hours. The solid is filtered at 50°C, washed with 50 ml of dimethylacetamide and 150 ml of methanol, then dried at 90°C under vacuum. 7,7 g of a red powder are obtained.

EXAMPLE 104

A mixture of 2,05 g of N,N'-bis(tert-butoxycarbonyl)-trans-2,2'-bis(4H-1,4-benzothiazine)-indigo from example 27 and 2 g of N,N'-bis(tert-butoxycarbonyl)-quinacridone (prepared as described in the example 27, replacing the thiazine-indigo with quinacridone) in 250 ml of

toluene is refluxed. Then 1,5g of para-toluenesulfonic acid monohydrate is added. The mixture is refluxed 30 mn further. The solid is filtered, washed with 120 ml of toluene and 80 ml of methanol, then dried at 90°C under vacuum. 2,38 g of a red powder are obtained.

EXAMPLE 105

A mixture of 310 ml of dimethylsulfoxide and 14,5 ml of sodium hydroxide 32 % is heated to 45°C. Then 12 g of 1,4-diketo-3,6-di(4-chlorophenyl)-pyrrolo[3,4-c]pyrrole and 12 g of trans-2,2'-bis(4H-1,4-benzothiazine)-indigo are introduced in the alkaline solution. The mixture is then heated at 85°C for 30mn. The hot alkaline solution is transferred into another reactor containing 700 ml of methanol at 25°C. The suspension of pigment is then refluxed for 3 hours and filtered, washed with 400 ml of methanol, 600 ml of water, then dried at 90°C under vacuum. 21,3 g of a red powder are obtained.

EXAMPLE 106

10,7 g of 1,4-diketo-3,6-di(4-chlorophenyl)-pyrrolo[3,4-c]pyrrole and 9,8 g of trans-2,2'-bis(4H-1,4-benzothiazine)-indigo are introduced in a reactor containing 200 ml of 96% concentrated sulfuric acid at 20°C. At the end of the introduction, a fine dark red suspension of pigment is obtained. The mixture is stirred for 4 hours at 20°C. Then the pigment is precipitated in 600 ml of water and heated 35°C for one hour. The suspension of pigment is then filtered and washed out with water, and dried at 90°C under vacuum. 18,55 g of a red powder is obtained.

APPLICATION IN PVC MASSTONE

The preparation of a 1% colored PVC sheet is performed following the DIN 53775A procedure:

100 parts of clear PVC are mixed with 1 part of pigment (obtained according to Example 1) for 2 minutes. The mixture is passed between two rollers for 5 minutes, the front roller being heated at 178°C and the rear roller being heated at 163°C. The PVC sheet is then treated again between the two rollers heated at 80°C. Then the sheet is pressed under a pressure of 30

tonnes between two chromium-plated steel plates heated at 165°C, for 30 seconds. The pressed sheet is colored with an orange shade.

APPLICATION IN PVC WHITE

The preparation of a 0.5% colored PVC sheet is performed following the DIN 53775B procedure:

100 parts of PVC-white (5% TiO₂) are mixed with 0.6 part of pigment for 2 minutes. The mixture is passed between two rollers for 5 minutes, the front roller being heated at 178°C and the rear roller being heated at 163°C. The PVC sheet is then treated again between the two rollers heated at 80°C. Then the sheet is pressed under a pressure of 30 tonnes between two chromium-plated steel plates heated at 165°C, for 30 seconds.

APPLICATION IN LACQUERS MASSTONE

The preparation of the alkyd-melamine-formaldehyde (AMF) resin coating is performed following the DIN 53235-1, DIN 8780/2 and 8781/1 procedures:

8 parts of pigment, 72 parts of clear AMF (BASF FF68-0102 14071) and 250 parts of glass beads are stirred in a Skandex stirrer for 10 minutes. 5 parts of this preparation are mixed with 5 parts of clear AMF (BASF FF68-0102 14071). The dispersion is sprayed on a cardboard sheet, air-dried for 10 minutes and baked at 130°C in an oven for 30 minutes.

APPLICATION IN LACQUERS WHITE

The preparation of the alkyd-melamine-formaldehyde (AMF) resin coating is performed following the DIN 53235-1, DIN 8780/2 and 8781/1 procedures:

8 parts of pigment, 72 parts of clear AMF (BASF FF68-0102 14071) and 250 parts of glass beads are stirred in a Skandex stirrer for 10 minutes. 3 parts of this preparation are mixed with 25 parts of AMF-white (BASF FD68-0410 11074). The dispersion is sprayed on a cardboard sheet, air-dried for 10 minutes and baked at 130°C in an oven for 30 minutes.

The pigments prepared in comparative Examples X and Y are compared with the pigment prepared in Example 1. The colorimetric measurements are reported in Tables I and II, and clearly show that the new process gives a cleaner product.

TABLE I: CIELAB MEASUREMENTS IN PVC AGAINST EXAMPLE 1

		PVC	Masstone			PVC	white	
<u>Ex.</u>	DE*	DH*	DC*	DL*	DE*	DH*	DC*	DL*
Ex. X	6.51	-2.5 redder	-6.02 duller	-3.47 darker	3.95	-2.69	-2.89	-1.61
Ex. Y	3.59	-1.92 redder	-3.03 duller	-2.18 darker	3.26	-2.73	-1.78	-1.19

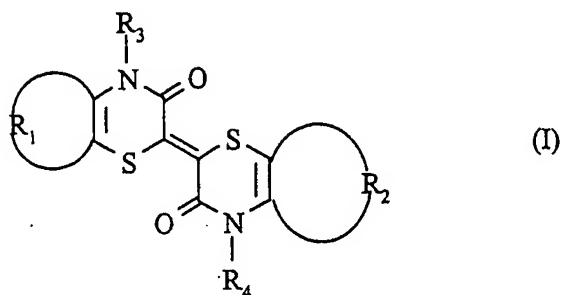
TABLE II: CIELAB MEASUREMENTS IN LACQUER AGAINST EXAMPLE 1

		Lacquer	Masstone			Lacquer	white	
<u>Exp.</u>	DE*	DH*	DC*	DL*	DE*	DH*	DC*	DL*
Ex. X	10.75	-2.99	-10.33	-4.6	2.75	-1.87	2.02	-0.59
Ex. Y	6.14	-2.01	-5.8	-2.72	1.59	-1.38	-0.79	1.06

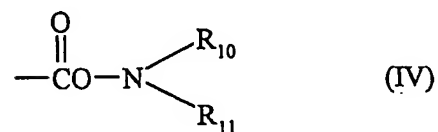
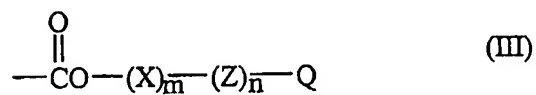
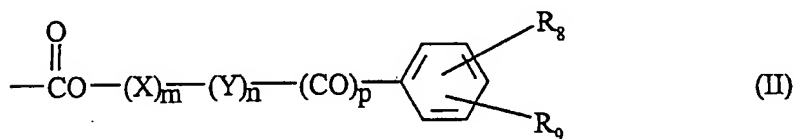
DH*, DC* and DL* are the colorimetric coordinates in the polar system L*, C* and H* of the CIELAB system. In these measurements, the point that represents the product Example 1 in lacquer or PVC is taken as the origin of the axes. So that these figures show the difference between Example X and 1, and Example Y and 1. A negative value of DC* means products X and Y are duller than Example 1 in PVC or lacquer.

CLAIMS

1. A pigment which is a compound of the formula (I)



wherein R_1 and R_2 are independently the atoms necessary to complete the formation of a substituted or unsubstituted aromatic or aliphatic carbocyclic or heterocyclic ring system, the radicals R_3 and R_4 , indepently of each other, are hydrogen or a group of the formulae (II), (III) or (IV)



whereby in the formulae (II), (III) and (IV)

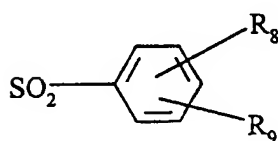
m , n und p , independently of each other, are zero or 1;

X C_{1-14} -alkylen or C_{2-8} -alkenylen;

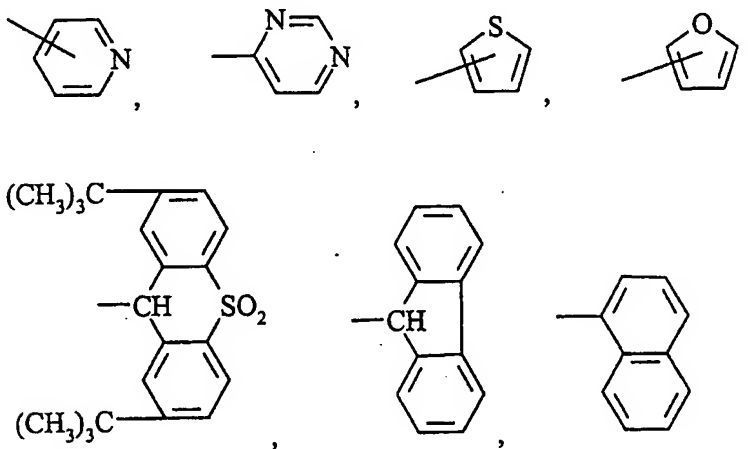
Y a group $-V-(CH_2)_q-$;

Z a group $-V-(CH_2)_r-$;

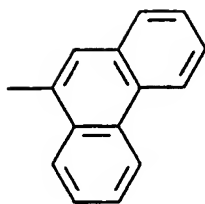
- V C_{3-6} -cycloalkylen;
 q a number of 1 to 6; and
 r a number of zero to 6,
 R_8 and R_9 independently of each other, signify hydrogen, C_{1-6} -alkyl, C_{1-4} -alkoxy, halogen, CN, NO_2 , unsubstituted phenyl or phenoxy, phenyl or phenoxy substituted by C_{1-4} -alkyl, C_{1-4} -alkoxy or halogen;
 Q hydrogen, CN, $Si(R_8)_3$, a group $C(R_{12})(R_{13})(R_{14})$, in which R_{12} , R_{13} and R_{14} are halogen; a group



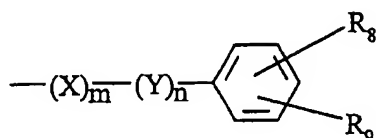
in which R_8 and R_9 have the above meaning; a group SO_2-R_{15} or SR_{15} , in which R_{15} is C_{1-4} -alkyl; a group $CH(R_{16})_2$, in which R_{16} is unsubstituted phenyl or phenyl substituted by C_{1-4} -alkyl, C_{1-4} -alkoxy or halogen; or a group of the formula



or



R_{10} und R_{11} independently of each other, signify hydrogen, C_{1-18} -alkyl, a group

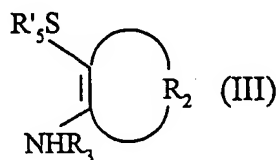
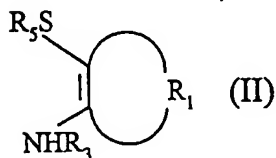


in which X, Y, R_8 , R_9 , m and n have the above meaning, or

R_{10} und R_{11} , together with the nitrogen atom to which they are bound, build a pyrrolidinyl-, piperidinyl- or morpholinylrest,

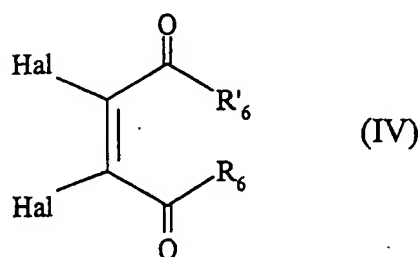
provided that, if R_3 and/or R_4 are a group of the formula (III), Q is hydrogen and n is zero, m must be 1 and X a C_{2-14} -alkylen- or C_{2-8} -alkenylengroup which is branched at the carbon atom bound to oxygen, and if both R_3 and R_4 are hydrogen, R_1 and R_2 cannot be identical.

2. A process of forming thiazine indigo pigments according to the formula (I) as defined in claim 1 comprising the step of reacting in the presence of a solvent system comprising a carboxylic acid and an inert polar aprotic solvent, a compound of formula (II) and a compound of formula (III)



wherein R_3 and R'_3 independently are H or a metallic ion selected from Na^+ , K^+ or Zn^{2+}

with a compound of formula (IV) [in its cis- or trans-form]



wherein Hal is F, Cl or Br, R₆ and R'₆ independently of the other is a leaving group commonly used in substitution reactions at carbonyl carbon atoms, e.g. Cl or alkoxy or together X and X' represent an oxygen atom.

3. A process according to claim 2 wherein the carboxylic acid is acetic acid.
4. A process according to claim 2 or 3 wherein the polar aprotic solvent is dimethylformamide.
5. A process according to any one of the preceding claims 2 to 4 wherein the solvent system consists of 5 to 95% by weight of carboxylic acid and 95 to 5% by weight of polar aprotic solvent.
6. A solid solution or a mixture of a thiazine indigo pigment according to formula (I) and another pigment of the class comprising diketopyrrolo-pyrrole, quinacridone, anthraquinone, benzimidazole, naphthole AS, azo condensation, isoindolinone, isoindoline, perylene, dioxazine, indigo, thioindigo, metal complex, perinone, quinophthalone and phthalocyanine pigments.

7. A method of using a pigment according to Formula (I) as defined in claim 1, a solid solution or a mixture as claimed in claim 6 for the mass pigmentation of substrates, preferably synthetic polymers, synthetic resins and regenerated fibers.
8. A method of using a pigment according to formula (I) as defined in claim 1, a solid solution or a mixture as claimed in claim 6 as a colorant for printing inks or textiles.
9. Synthetic polymers, synthetic resins and regenerated fibers comprising a pigment according to formula (I) as defined in claim 1, a solid solution or mixture as claimed in claim 6.
10. Printing inks or printed textiles comprising a pigment according to formula (I) as defined in claim 1 or a solid solution or mixture as claimed in claim 6.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 98/00109

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09B7/00 C09B67/22 C08K5/46 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 803 139 A (KAUL B) 9 April 1974 see example 4 & DE 21 51 723 A cited in the application ---	2-5
A	DE 25 36 120 A (BASF AG) 3 March 1977 cited in the application see examples ---	1-10
A	EP 0 648 770 A (CIBA GEIGY AG) 19 April 1995 cited in the application see claims; examples ---	1-10
A	EP 0 654 506 A (CIBA GEIGY AG) 24 May 1995 see claims -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

21 April 1998

Date of mailing of the international search report

06/05/1998

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Authorized officer

Ginoux, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .onal Application No

PCT/IB 98/00109

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US 3803139 A	09-04-74	CH 549626 A BE 774283 A DE 2151723 A FR 2111606 A GB 1358574 A	31-05-74 14-02-72 27-04-72 02-06-72 03-07-74
DE 2536120 A	03-03-77	NONE	
EP 0648770 A	19-04-95	CA 2117865 A JP 7188234 A US 5484943 A US 5616725 A CA 2152744 A EP 0690057 A JP 8027391 A US 5591865 A CA 2152745 A EP 0690058 A JP 8048908 A US 5650520 A CA 2152748 A EP 0690059 A JP 8020731 A US 5646299 A	14-04-95 25-07-95 16-01-96 01-04-97 30-12-95 03-01-96 30-01-96 07-01-97 30-12-95 03-01-96 20-02-96 22-07-97 30-12-95 03-01-96 23-01-96 08-07-97
EP 0654506 A	24-05-95	CA 2135596 A JP 7196939 A US 5518539 A	23-05-95 01-08-95 21-05-96